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ABSTRACT

An experimental apparatus was designed and constructed to utilize high vacuum and mass spectrometric techniques to determine total and partial vapor pressures above bulk liquid samples in the temperature range between -65°C and 25°C.

Observations on the sulfuric acid-water system revealed complexities which interfered with the experimental goal, but which are of some interest in themselves. These interfering processes included long internal thermal relaxation times and chemical reactions. An unexpected and most interesting observation was an apparent pressure effect on the melting curve of the sulfuric acid-water mixtures. The main result of this study is a description of this apparent pressure effect.

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SECTION 1

INTRODUCTION

The main purpose of this research was to directly measure the very low vapor pressures of fluid mixtures which, in low concentrations, form aerosols in the ambient atmosphere. The prime example of such a system, and the one deemed most important in this study, is the mixture of sulfuric acid and water. As originally submitted, our proposal for this work foresaw successful measurements on the sulfuric acid-water system (subsequently H_2SO_4 - H_2O) and sufficient understanding of it to allow for expanded studies of other systems, including other inorganic acids as mixture components, and even of organic compounds such as are found in automobile exhausts. Unavoidable delays in completion of the experimental apparatus, and unexpected complexities in the H_2SO_4 - H_2O system, precluded attainment of this program. In the following, attention is restricted to the single system upon which measurements were actually made in the apparatus, that being H_2SO_4 - H_2O.

An extensive literature[1-9] attests to long scientific interest in the chemistry and thermodynamics of H_2SO_4 - H_2O. However, no direct measurements of vapor pressure of H_2SO_4 - H_2O in the interesting region near 100% H_2SO_4 have been published. This is not very surprising, due to the extremely low value of this pressure and the difficulty of accurately measuring low pressures. The 1970's brought increasing attention to the role of the formation of H_2SO_4 and other sulfates in air pollution. This provided the incentive for new attempts to directly measure the relevant physical-chemical processes involved.

Thus followed the present attempt to design an apparatus by which the expected very low values of the equilibrium vapor pressures could be measured above the surface of bulk H_2SO_4 - H_2O. Because pressure gradients are easily established along tubes and across apertures at the low pressures being considered, a vacuum chamber was designed so that the pressure-measuring devices (nude ion gage, capacitance manometers, and the ion-source region of a mass spectrometer) would be located physically as close as possible to the sample. Especially, it was desired to minimize obstructions to vapor motion between the sample and the measuring devices. This consideration, as well as the requirement of sample cooling equipment in order to study the temperature behavior, resulted in a rather large ($\sim 0.06\ m^3$) vacuum chamber. It was understood at the outset that this large a vacuum chamber could result in relatively long equilibrium times. However, this was outweighed by the resulting simplicity of design and minimization of pressure-gradient and mass-discriminating effects in the apparatus.

It may be noted at this point that a Knudsen-cell-type design was also considered. (In a Knudsen cell the sample is completely enclosed except for a pin hole through which vapor may escape. Under low-pressure molecular flow conditions, the intensity of the molecular beam exiting the pin hole is related to the vapor pressure of the sample). This was rejected as leading to a design of considerably greater complexity than the present one. Also, the Knudsen pin hole is itself a mass-discriminating device, and thus corrections would have to be applied in order to estimate the partial pressures of the mixture systems.

Other criteria which the design was to meet were the following: (1) the ability to measure total pressures in the range from atmospheric pressure ($\sim$ 100 kPa) to the lowest estimate as found in the literature for the vapor pressure of pure H_2SO_4 ($\sim 10^{-6} - 10^{-5}$ Pa), (2) temperature measurement and control from approximately room temperature (25°C) to the low temperatures found in the stratosphere ($\sim$ -65°C), and (3) the ability to detect and measure the relative concentrations of various mixture components in the vapor. For this a mass spectrometer was incorporated into the design. Construction of the experimental apparatus began with receipt of the first of the instruments ordered in May of 1975.

Reliable operation of the entire apparatus in its final form was attained in May of 1977. Most of the experimental data reported here were obtained during the period from May to August, 1977. Exceptions are certain preliminary measurements and calibration measurements which were accomplished prior to this period.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The main purpose for which this apparatus was constructed, namely the direct measurement of the total vapor pressures and the partial equilibrium vapor pressures of sulfuric acid-water mixtures (H_2SO_4 - H_2O) has proved to be an elusive goal. Several factors contributed to this lack of success, but one major reason is the presence of a very interesting but completely unexpected complication: an apparent pressure effect on the melting curve of H_2SO_4 - H_2O.

The strongest evidence for this pressure effect on the melting curve was seen in the H_2SO_4 - H_2O samples at concentrations near that of the monohydrate (84.5 wt% H_2SO_4). In particular, the experimental runs of July 7 and July 11, 1977 indicate a reproducible difference of 15°C between the melting temperature of this mixture at near-atmospheric pressures (60 to 80 kPa) and pressures of the order of 1.0 Pa. Reproducibility of the melting point reduction upon temperature and pressure cycling shows that the effect cannot be the result of distillation in the pumping process, which would lead to changes in the composition of the sample. In particular the reproduction of the "high pressure melting point" following an observation of the "low pressure melting point" in the sample of July 11, 1977 indicates that the mean concentration of the sample was not significantly changed during that day's run.

The observations of melting in samples with nominal concentrations of 96.5 and 100 wt% H_2SO_4 are not inconsistent with the existence of a possible pressure effect on the melting curve. However, the conclusions in these cases are made ambiguous by the effects of persistent supercooling, possible dissolved gases, and possible, as yet unidentified, chemical reactions. The latter two effects are also major obstacles to overcome if the original intention of measuring the vapor pressure in this system is to be attained.

It is the opinion of the authors that at this point the most pressing problem is the further elucidation of the nature of the apparent pressure effect on the melting curve in H_2SO_4 - H_2O. The existence of the effect requires confirmation and corroboration by further experiment, and a detailed determination of the extent of melting point lowering with pressure is imperative. Assuming for the moment that the apparent pressure effect on the melting curve is corroborated by further experiment, then the thermodynamic consequences of the effect must be explored. This would include possible extensive modification of calculations such as those by Gmitro and Vermeulen.[5]

It may, of course, prove to be the case that this apparent effect is due to impurity gases, supercooling effects, or is in some other way an unforeseen experimental artifact. Even so, the course of the effect must be resolved in order that further progress be made towards a direct measurement of the vapor pressures in the system.

Results of the mass spectrometric observations on this system remain at this point purely qualitative, and even somewhat tentative. However, this has not been a major limiting factor in the experimental analysis. Further work in this direction appears to hold some promise in elucidating the physical and chemical behavior of the H_2SO_4 - H_2O system.

SECTION 3

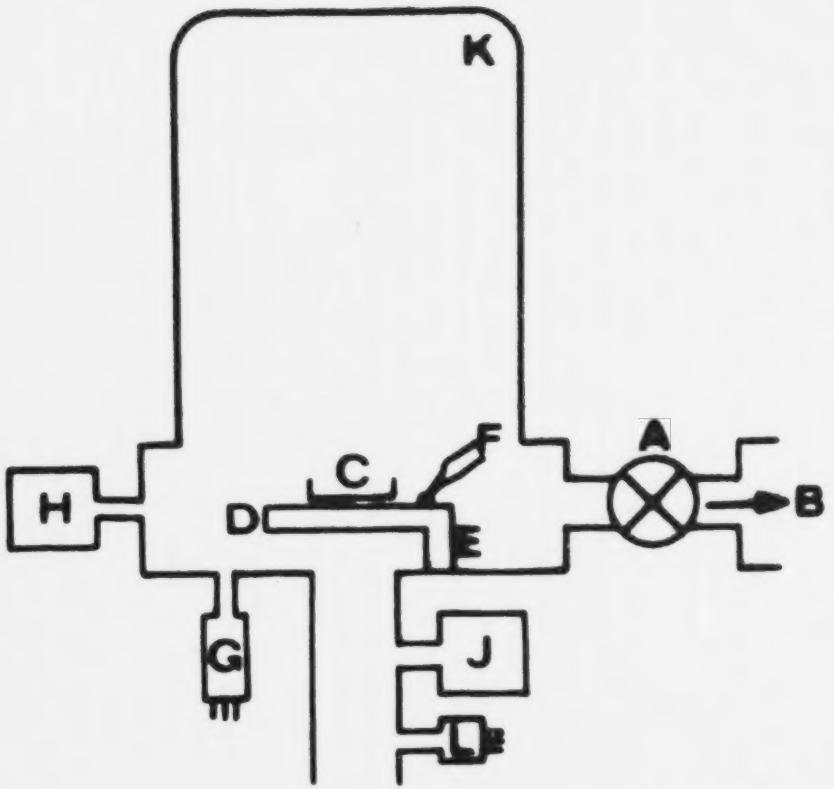
DESCRIPTION OF THE APPARATUS

GENERAL

A sketch of the experimental apparatus, showing the spatial relationships between the various measuring instruments, is given in Figure 1. In the text below, capital letters in parentheses refer to items identified in Figure 1.

A sample dish containing the H_2SO_4 - H_2O liquid is supported inside the vacuum chamber by a stainless steel, temperature-controlled table (D). This table is cooled and its temperature controlled by chilled alcohol from a circulating bath refrigerator (Neslabs Model LT-9). The chilled alcohol enters the vacuum chamber through the feedthrough (E), is routed to the interior of the cooling table via stainless-steel tubing, circulates through the interior of the cooling table, is drained by the re-entrant section of the same feedthrough (E), and is returned to the circulating bath refrigerator. This system provided temperature control to within ± 1°C throughout the temperature range -60°C to +10°C. During the period in which most of the data reported here were taken, operation was limited to a lower temperature of -35°C. This was due to a malfunction of the circulating bath refrigerator followed by an improvised repair. The decision was made to operate the system within the limited temperature range rather than suffering a six- to eight-week hiatus while the refrigerator was returned to the factory for proper repair. The cooling table itself was the source of considerable difficulty, in that the first model of this table proved to be of poor quality. The facilities of the shop where the table was made were insufficient to insure that the extensive welding required was vacuum-tight. After a few thermal cycles, persistent and ever more numerous leaks developed in this table. Eventually it was necessary to contract with the Georgia Institute of Technology Research shop to construct a second model of the cooling table. The second model proved to be quite adequate, and provided trouble-free service.

The temperature of the cooling table was monitored by a chromel-gold (2% iron) thermocouple, which is the sensing element in a Lakeshore Cryotronics, Inc. Model DRC-5 thermometer. This device incorporates an internal electronic standard which makes its use extremely convenient and trouble-free in this application. (I.e., no reference junction maintained at a fixed-point temperature is needed.) This thermometer could detect temperature changes of ± 0.2°C, and was stable for short periods (∿ 30 minutes) to within ± 0.5°C. The thermocouple itself was embedded within epoxy in a blind hole 3.2 mm in diameter and 3.2 mm deep drilled in the stainless steel cooling table. The epoxy provided a mechanically strong, thermally conducting and electrically



A Vacuum Valve
B To Mass Spectrometer
C Pyrex Sample Dish
D Temperature Controlled Table
E Table Coolant Inlet
F Thermocouple
G Ion Gauge
H Manometer 0 - 133 Pa
J Manometer 0 - 133 kPa
K Bell Jar
L Thermocouple Vacuum Gauge

Figure 1. Experimental Apparatus.

insulating bond between the thermocouple and the cooling table.

The vacuum chamber was pumped via a pumping line 10.16 centimeters in diameter by a CVC Products, Inc., Model PMC-4B diffusion pump. The pump was charged with polyphenyl ether oil, and the pumping line contained a liquid-nitrogen-cooled baffle. This system was capable of producing a bell jar pressure of 10^{-6} Pa when the freshly cleaned vacuum chamber contained no sample and was pumped overnight.

Four independent pressure-sensing devices were used to monitor the total pressure inside the bell jar. One of these was the thermocouple vacuum gauge (L), which was used only to monitor the operation of the vacuum pump, and which played no part in the experimental measurements.

The primary instruments for total pressure measurements in this experiment were two capacitance manometers. These devices sense the changes in capacitance when the system pressure flexes a thin metal membrane which forms one half of a flat-plate capacitor. This type of manometer is directly sensitive to force per unit area. Thus it measures pressure directly, and is not sensitive to the composition of the gas or mixture of gases which produce the pressure. The manometers used here are the Baratron Model 145A, manufactured by MKS Instruments, Inc. Two manometer sensing heads were used, a high-pressure one (J) for the range 0 - 133 kPa and a low-pressure one (H) for the pressure range 0 - 133 Pa. Pressure differences of 2×10^{-5} of the range could be detected with these instruments, and the readings were reproducible to within 50% at 10^{-4} of the range. Thus the two sensing heads provided direct measurement of the pressure throughout the range from atmospheric pressure to 10^{-3} Pa.

Finally an ionization gauge (G) inside the bell jar allowed measurements of total pressures below 10^{-2} Pa to the ultimate vacuum attainable within the system. This ionization gauge is "nude", i.e., the filament, collector and heater that constitute the sensing element project from the wall of the bell jar to the region near the sample, rather than being enclosed in tubulation projecting out from the bell jar wall. This construction was used in order to minimize any possible pressure gradient between the sample and the ion gauge.

The ion gauge has the advantages of excellent sensitivity, precision and reproducibility. Unfortunately, its response varies with the chemical identity of the gas. This leads to large uncertainties (factors of two to ten) in the absolute pressure as measured by this instrument for different gas mixtures. It was our original intention to calibrate the response of the ion gauge to each gas mixture used in this experiment by relating the ion gauge readings to those of the low-pressure capacitance manometer where their ranges overlapped; i.e., 10^{-2} - 10^{-3} Pa. During our study of the H_2SO_4 - H_2O system the necessity for this procedure never arose, as pressures in the range below 10^{-2} Pa were not attained while the sample was in the system.

In order to detect and measure the concentrations of the various chemical species in the vapor above our samples, a mass spectrometer was made a part of the apparatus. The sensing element of the mass spectrometer (B)

could communicate with the sample space through a stainless steel tube with an inner diameter of $\sim$ 4.5 cm and a length of $\sim$ 30 cm. A large valve (A) controlled communication between the mass spectrometer and the bell jar. (This valve, which is referred to as Valve "A" below, has a maximum aperture of $\sim$ 5 cm.) The tube connecting the bell jar and the mass spectrometer was fashioned to be as short and as large in diameter as was physically possible, again to minimize pressure gradients. This tube could be heated to reduce the possibility of condensation between the bell jar and the mass spectrometer.

The mass spectrometer itself is a time-of-flight instrument, Model MA-3A, manufactured by CVC Products, Inc. It has a completely independent vacuum pumping system. Ionization is accomplished by electron impact in the source region of the instrument; the ions are then accelerated by an electric field and allowed to drift. More massive ions are accelerated less by the field, and so the ions are segregated by mass as they drift. High speed detection and counting of the ions thus provides a mass spectrum of the original gas. This instrument is sensitive to molecules in the mass range from one to approximately six hundred atomic mass units, and has a resolution of $\frac{m}{\Delta m} = 300$ at m = 200 AMU.

Two systems were used to monitor the output of the mass spectrometer analyzer: an oscilloscope in one channel, and an electronic scanner with a chart recorder in another channel.

The oscilloscope used was a Tektronix Model 5403. The oscilloscope was used to provide an easily observed overview of the mass spectrum. This capability is a requirement for convenient tuning of the mass spectrometer. Also it allowed one to visually, and therefore quickly, note regions of the spectra of particular interest, occasional transient phenomena in the spectra, and immediate indication of anything wrong with the mass spectrometer. The oscilloscope channel is not convenient for providing a permanent record of data.

The other channel, that containing the scanner, utilizes a gate to select a small segment of the total mass spectrum from each sweep of the mass spectrometer. (The instrument produces approximately 30,000 "sweeps" each second during operation.) The width of this gated segment was usually set to be a small fraction of the width of a single mass peak. The signal in the gated segment could be integrated over many sweeps of the spectrometer, thus providing excellent sensitivity. Controls on the scanner allow the gate to be moved through the spectrum at will, and for the gate width, scan rate and scan range to be varied. Thus any part of the mass spectrum can be closely scrutinized using the scanner. This scanner is a CVC Products, Inc., Model 010. The signal from the scanner is amplified within the scanner itself and displayed on a meter as a direct-current voltage. This voltage is also supplied to a chart recorder, in this case an L & N Model 625, to provide a permanent record of the mass spectra as scanned by the instrument.

INSTRUMENT CALIBRATIONS

Since the available facilities for calibration of pressure and temperature sensors was extremely limited, care was taken to procure only those devices which could be delivered with a factory-certified calibration. This was one consideration in buying the thermocouple thermometer and the capacitance manometers. (The ionization gauge could not be so certified, by the nature of the instrument. Our intended procedure for calibrating this instrument with the low-pressure capacitance manometer is briefly described above. As noted there, the necessity for this calibration did not arise in the experiment).

The thermocouple thermometer contained an internal electronic standard which related the potential difference produced by the thermocouple to the Kelvin temperature, which was digitally displayed by the instrument. This standard could however be "shifted" by a bias voltage. Before installation into the apparatus this voltage was set to provide a reading of 273.12 ± 0.50K when the thermocouple was submerged in an ice-point bath. This bias setting was then checked by dipping the thermocouple into liquid nitrogen, and noting that the thermometer displayed the correct value of this temperature as 77 K.

Installation of the thermocouple sensor into the vacuum chamber involved two solder joints in each of the thermocouple leads. After the thermocouple was installed it was noted that readings of room temperature by the thermometer appeared to be too high by some three or four degrees, as compared to a mercury-in-glass thermometer. This shift was confirmed by data taken in the system on the vapor pressure of pure water. The pure-water runs are described in greater detail below. It was found that the initial readings of the vapor pressure of pure water as a function of temperature would agree with the accepted values only after a downward shift of the recorded temperatures by 3.8 degrees. The thermometer bias voltage was adjusted to provide this shift. Subsequent measurements of the pure-water vapor pressure were always found to agree with the accepted values.

The pure water vapor pressure runs were also confirmation of the calibration of the capacitance manometers. These manometers did show a small day-to-day drift in the reading for "zero" pressure. This drift was typically 3×10^{-4} of the instrument range. Small daily adjustments of a bias voltage to reset the zero for these instruments was part of the routine during data collection. So long as care was taken to reset the zero readings, no discrepancy was found between the two capacitance manometers when they were each exposed to the same system pressure. This could, of course, only be noted within the range of the low-pressure capacitance manometer.

SECTION 4

EXPERIMENTAL MEASUREMENTS

PURE H_2O RUNS; AND GENERAL SAMPLE HANDLING PROCEDURES

As a final check out of instrument calibrations and general system performance several data runs were made on the pure water system. The pure water system is also, of course, an important limiting case of the H_2SO_4 - H_2O system, and thus it was important to measure the ability of the apparatus to reproduce the well-known vapor pressure curve of water.

Most of the sample handling techniques were similar for all sample runs and that will be described here.

Pure distilled water (Fisher Reagent W-2) was poured into a clean sample dish. The sample dish and the sample were then immediately lowered to the surface of liquid nitrogen in a dewar, thereby becoming solidly frozen at a temperature of 77 K. At this temperature the vapor pressure of water is negligibly small, and that of H_2SO_4 - H_2O is even considerably less than that of pure water. Thus a frozen sample at this temperature could be safely pumped from atmospheric pressure to high vacuum with no danger of distillation causing changes in the sample composition.

Meanwhile the cooling table inside the bell jar was refrigerated to its lowest temperature (-65°C in early runs and -35°C after difficulties developed with the refrigerator). The pressure inside the bell jar was increased to atmospheric pressure by venting with high purity dry nitrogen gas. The dry nitrogen gas was allowed to continue flowing into the bell jar as the vacuum space was opened to permit the admission of the experimental sample. Thus a slight dynamic over pressure of dry nitrogen gas was maintained in the vacuum chamber volume as the sample was introduced. This procedure minimized the introduction of ambient air into the system along with the sample. There was particular concern not to introduce atmospheric water vapor with samples containing high concentrations of H_2SO_4, since these samples are extremely hygroscopic.

Thus a solidly frozen sample was introduced under an inert, dry nitrogen atmosphere and placed on the cooling table at its lowest temperature. The bell jar was then closed and the vacuum chamber evacuated as quickly as possible.

The system was pumped down until the pressure was well below that expected as the equilibrium value for the sample at the cooling table temperature.

When this point was reached, the pumping aperture was closed, and the system was allowed to come to pressure equilibrium. Here "pressure equilibrium" was operationally defined as having been reached when no change was noted in the pressure reading during a reasonable observation time - generally five to ten minutes. Typically then the reading of the pressure and temperature would be recorded, and the temperature of the cooling table increased by whatever increment was desired to reach the next intended temperature.

By this process we were able to reproduce the accepted vapor-pressure curve of pure water throughout the temperature range of $-30^{o}C$ to $+15^{o}C$, corresponding to vapor pressure between 40 Pa and 1500 Pa. Data from one such pure water run are shown in Fig. 2.

Long equilibrium times were of considerable concern in the experiment. In the measurements on the pure water system it was found that for the higher pressures (above 1 kPa), equilibrium times as observed in the apparatus were always negligibly short (< 100 sec). A limiting factor in determining the high pressure equilibrium times was the fact that the system temperature would respond to small changes in the room temperature. At the lowest pressures in the pure water runs, the equilibrium times became quite long, on the order of one hour. As a result of the experience with the pure water system in the apparatus, we were prepared to find that long equilibrium times would be a limiting factor in our ability to accurately measure total vapor pressure in the H_2SO_4 - H_2O system, particularly at high concentrations of H_2SO_4. However this did not prove to be the case. As described below, complexities within the H_2SO_4 - H_2O system itself proved to be the limiting factors.

PRESSURE-TEMPERATURE RUNS ON SAMPLES NEAR 100% H_2SO_4

Two commercially available formulations of H_2O - H_2SO_4 were used to prepare the samples. These are:

Fisher A-300 : 95 - 98 wt% of H_2SO_4 and

Fisher A-304 : Sulfuric Acid Fuming, 15-18 wt% excess SO_3

In the case of H_2SO_4 - H_2O it is reasonable to talk of mixtures containing a weight percentage of H_2SO_4 greater than one hundred. This can come about due to the fact that the acid molecule can undergo the dissociation:

$$H_2SO_4 \rightarrow H_2O + SO_3$$

Removal of H_2O molecules increases the concentration of the acid, and removal to the point of an excess of SO_3 corresponds (by convention) to a concentration of H_2SO_4 in excess of 100%. The weight percentage of H_2SO_4 is then always simply related to the weight percentage of SO_3 by the ratio of the molecular weights:

$$\text{Wt\% } H_2SO_4 = (\text{Wt\% } SO_3)\ (98.082/80.066)$$

The A-304 commercial preparation can be seen to have a mean composition of 84.7 wt% SO_3, from which we determine the H_2SO_4 concentration:

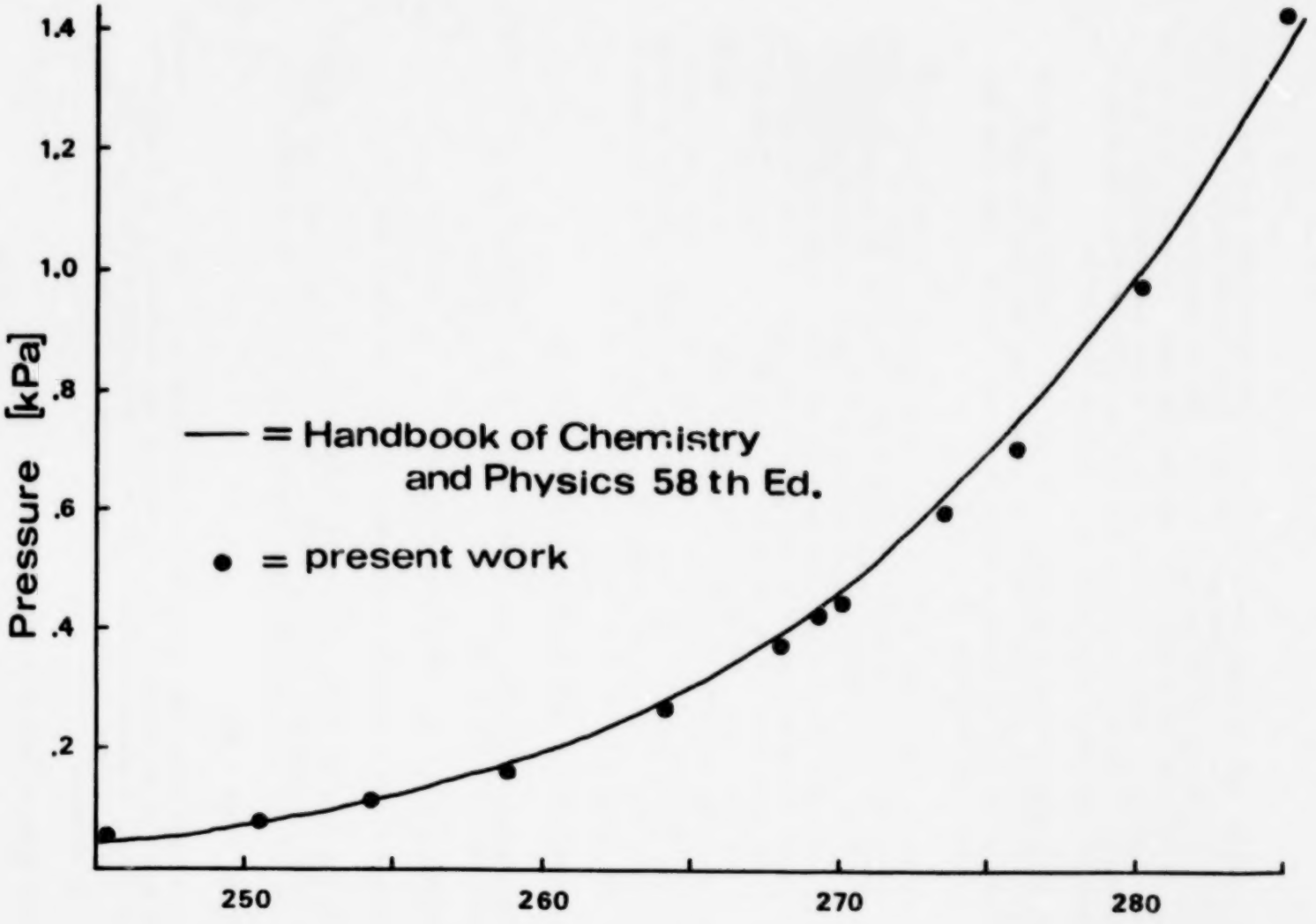


Figure 2. Vapor Pressure of Water.

Fisher A-304 : 103-104 wt% H_2SO_4

Thus, samples with concentrations in the range 95 < wt% H_2SO_4 < 104 could be produced by mixing A-300 and A-304 together. Since the variation of specific gravity between these two concentrations is negligible[10], a straightforward volumetric mixing can produce any desired concentration intermediate between A-300 and A-304.

Samples were prepared in this way such that 99 < Wt% H_2SO_4 < 101. These are referred to below as "100% H_2SO_4". The actual mixing was accomplished utilizing calibrated pipets to prepare approximately 2-ml samples of the desired mixture. As these high concentration samples are extremely hygroscopic, care was taken to minimize the time during which they were exposed to air. Typically the entire process of mixing the sample and getting it under a dry nitrogen atmosphere at 77 K required less than one minute.

Pressure-temperature runs were performed on A-300 samples and on 100% H_2SO_4 samples and these are described in this section. Observations using the mass spectrometer are given at the end of this section.

The initial runs on the A-300 and 100% H_2SO_4 samples produced very similar results, and these will be described together. A solidly frozen sample of 100% H_2SO_4 at 77 K was transfered under dry nitrogen atmosphere to the vacuum chamber cooling table, which was maintained at a temperature of 240 K. The bell jar was then quickly lowered to close the vacuum chamber and the vacuum space was evacuated as quickly as possible. Typically it was found that the vacuum system could not be pumped down below pressures less than about 0.4 Pa. If this figure were to represent the equilibrium vapor pressure it is surprisingly high, approximately two orders of magnitude larger than the estimates of Gmitro and Vermeulen for H_2SO_4 - H_2O in this concentration range. However the other observations described below strongly indicate that this can not be interpreted as an equilibrium vapor pressure.

As the pumping line was shut off, the pressure in the bell jar was noted to quickly rise to the neighborhood of 1.0 - 3.0 Pa, and then to more slowly increase at a rate not perceptively different from the leak-up rate observed when the vacuum chamber was empty of the sample. The solid sample, meanwhile, showed signs of local melting. In fact, bubbles were always noted which would rise and burst at the surface. This was not a totally unexpected observation, as it was suspected that some amounts of dissolved gases would be present in the sample, and that these could possibly cause local heating effects as they came out of solution. (At higher temperatures, the bubbling behavior could be noted to occur at higher pressures.)

An observation that was quite unexpected was that the areas of local melting did not refreeze, even though the temperature of the cooling table was far below the melting temperature of the sample. The relevant part of the melting curve in H_2SO_4 - H_2O is shown in Fig. 3. From this we see that the 100% H_2SO_4 sample has a melting point at 282 K and a 95 wt% H_2SO_4 sample would melt at approximately 250 K.

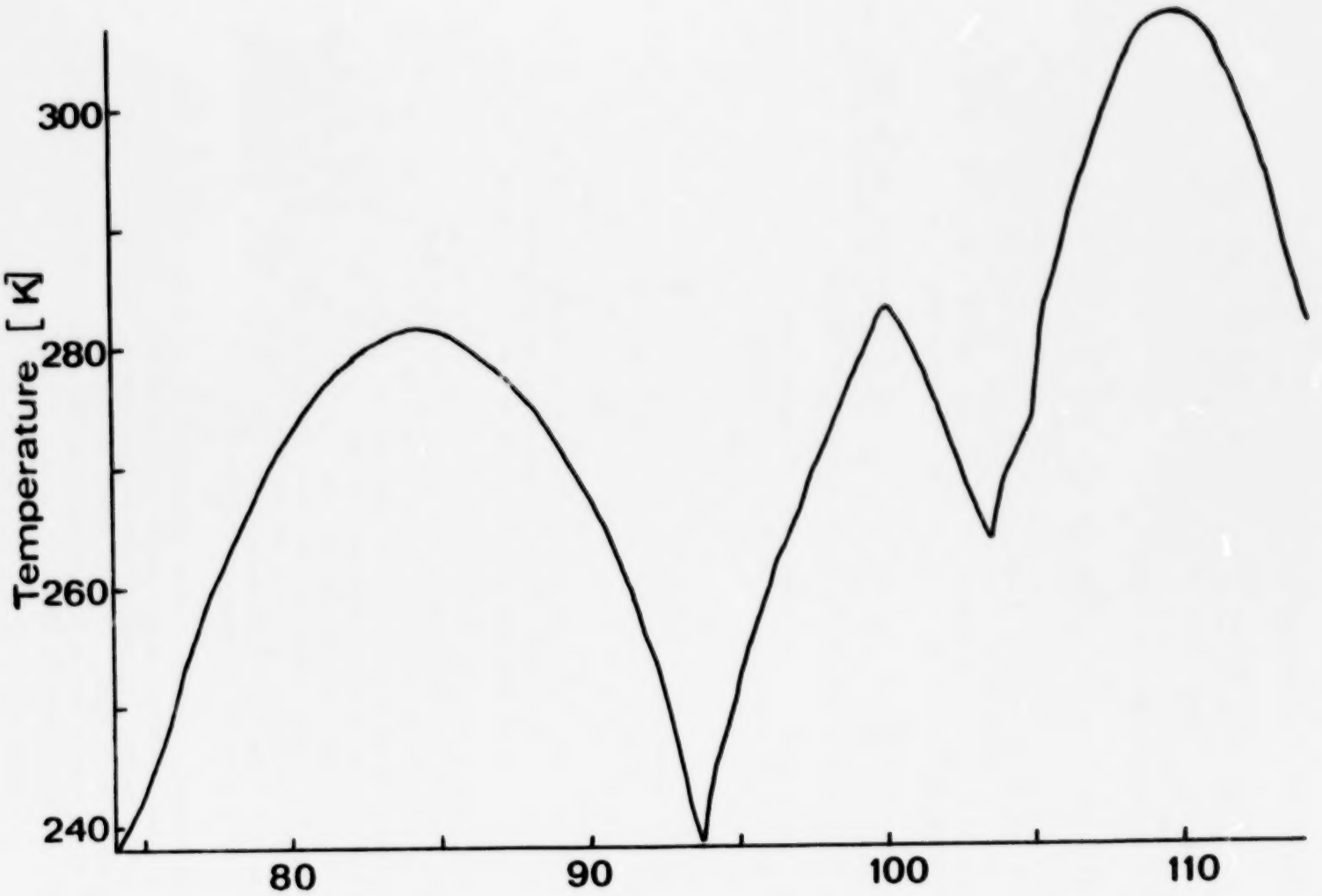


Figure 3. Melting Point of H_2SO_4 from Gable, Betz, and Maron (Ref. 3).

The sample would continue to melt, often forming porous solid structures that would coexist with the liquid for periods up to two hours in length. Eventually the sample would become completely melted and the liquid would be noted to take on a greenish color, which would darken as the sample aged. Two conclusions could immediately be drawn from these observations:

(i) The very long life times of porous and filamentatious solid coexisting with the liquid to which it was melting suggest that thermal equilibrium times within the sample itself were quite long, regardless of how rapidly external thermal equilibrium or quasi-equilibrium was obtained.

(ii) The greenish discoloration indicated that quite possibly some chemical process was proceeding.

Either of these conclusions would hamper the ability of the present technique to provide measurements of the equilibrium vapor pressure of H_2SO_4 - H_2O system.

The total melting of these 100% H_2SO_4 and A-300 samples at temperatures well below the melting curve was quite unexpected. From Fig. 3, only samples with concentrations between 93.5 - 94.0 wt% H_2SO_4 should be liquid at a temperature of 240 K. Distillation of the samples was discarded as a possible cause, as this would result in an increase in the concentration of H_2SO_4, rather than the needed decrease. Supercooling effects were considered as well, since it is known that these mixtures strongly supercool. However, thermodynamics does not permit the melting of an equilibrium solid to a supercooled liquid.

It proved to be exceedingly difficult to refreeze any of the high wt% H_2SO_4 samples after they had become completely melted -- this only occurred with one sample, a 100% H_2SO_4 sample. In this case, the pressure in the bell jar was very rapidly increased to atmospheric pressure with dry nitrogen gas, while the temperature of the cooling table and the melted 100% H_2SO_4 sample remained below 250 K. As the pressure reached approximately 93 kPa the sample suddenly refroze to its expected equilibrium solid. Several attempts to reproduce this behavior met with no success. In this isolated refreezing incident it appeared that the only parameter to have changed significantly was the external pressure, and thus there appeared to be some possible pressure effect on the melting curve.

For this reason, it was decided to make a series of measurements on samples of H_2SO_4 - H_2O with concentrations near that of the monohydrate, $H_2SO_4 \cdot H_2O$. The monohydrate mixture has a concentration of 84.5 wt% H_2SO_4. Reference to Fig. 3 indicates this concentration corresponds to a rather broad maximum in the melting curve, with the conveniently high melting temperature of 281 K. Thus the behavior of the system in this region is relatively insensitive to small changes in the concentration. Therefore any effect of pressure variation can be isolated with relative ease.

PRESSURE - MELTING POINT RUNS ON MONOHYDRATE SAMPLES

General

Samples with concentrations near that of the monohydrate, $H_2SO_4 \cdot H_2O$, were prepared by mixing distilled water with the A-300 sample acid, in the same manner as described previously. In this case a volume correction was necessary because of the large difference in specific gravity between pure water and the concentrated sulfuric acid. Two samples were prepared and runs were made on separate days. These runs will be described in detail.

Run of July 7, 1977

A sample with nominal concentration of 84.6 wt% sulfuric acid and a volume of 1.26 ml was prepared and immediately frozen at liquid nitrogen temperature. This was transferred under a dry N_2 atmosphere to the cooling table, which was maintained at a temperature of 256 K. The bell jar was only slightly evacuated, to a pressure of 81.6 kPa, simply to hold the bell jar down and isolate the sample from the ambient atmosphere.

The temperature of the cooling table was then raised in steps of roughly five degrees. At a temperature between 281 K and 282 K it was noted that the sample was in the process of melting. This agrees with the expected melting point, from Fig. 3 of 281.6 K for this sample. The sample completely melted before the temperature could be reduced again.

The cooling table temperature was reduced to 238 K but the sample supercooled and did not refreeze into solid. The bell jar was pumped down using the forepump. The forepump could not reduce the pressure over the supercooled sample to below 0.9 Pa. In an attempt to freeze the supercooled liquid, the pressure was increased to 38.7 kPa by introducing dry nitrogen gas, while maintaining a temperature of 238 K. A small crystal was then noted to appear in the sample, and this grew rapidly, causing the entire sample to transform to the crystalline solid within approximately ten minutes. After obtaining a solidly-frozen sample, the pumping line was again opened to the forepump. The system pressure was reduced to 0.48 Pa and could not be pumped below this value. The pumping line was again closed and the temperature increased in five degree steps.

The sample underwent the solid-to-liquid transition during one of the steps. The sample was noted to be roughly 50% melted at a temperature of 266 K and a pressure of 1.3 Pa. The observations of this run indicate the following:

(i) The system exhibits substantial supercooling. This is not unexpected behavior and is indicated in the literature.

(ii) Two distinct melting points were observed, the expected one at a temperature of 281 - 282 K and a pressure of 81.6 kPa, and an unexpected one at a temperature of approximately 266 K and a pressure of about 1.3 Pa.

One might assume that the pumping had distilled the water from the mixture, thus reducing the melting temperature. However, from Fig. 3, this would require an increase in concentration from 84 wt% to 90.5 wt% H_2SO_4. Distillation to this extent would appear to be highly unlikely under the experimental conditions. Also the observed melting pressure of about 1.3 Pa is difficult to reconcile with the pressure of $\sim 2.824 \times 10^{-4}$ Pa obtained from the tables of Gmitro and Vermeulen for H_2SO_4 - H_2O at 90.5 wt% H_2SO_4 and 266 K.

A second independent run on another sample near the monohydrate concentration appeared to be necessary in order to see if the behavior shown by the run of July 7, 1977 could be reproduced, to measure more carefully the transition temperatures and pressures, and to attempt to estimate the extent of possible distillation.

Run of July 11, 1977

A sample with a nominal concentration of 84 wt% H_2SO_4 and a volume of approximately 2.5 ml was prepared. The standard sample handling technique was observed, with the mixed sample quickly frozen at 77 K with liquid nitrogen and under a dry N_2 atmosphere transferred to the cooling table, which in this case was maintained at a temperature of 255 K. As before, the atmosphere within the bell jar was dry nitrogen gas.

The vacuum chamber was slightly pumped down to a pressure of 80.9 kPa. The pumping lines were closed off and the temperature of the cooling table slowly raised while the pressure and the sample appearance were monitored. The sample was observed to melt over a range of approximately eight degrees. The temperature, pressure and visual estimates of the extent of melting of the sample are given in Table 1.

TABLE 1. HIGH PRESSURE MELTING, MONOHYDRATE SAMPLE

T (K)	Pressure (kPa)	Extent of Sample Melting (Visual Estimation)
275.7	81.281	Barely discernable
279.1	81.349	20%
281.4	81.407	40 - 50%
282.4	81.424	50%
283.5	81.444	80 - 85%
283.9	81.460	90%

It was decided to term the "melting point" that temperature at which 50% of the sample was estimated to be in each of the solid and liquid states. By this criterion, the melting point of this sample was determined to be 282.0 ± 0.5 K. This is quite consistent with the value of 281.7 K taken from the melting curve (Fig. 3). This constitutes good assurance that this

sample is indeed within approximately 2% of the monohydrate concentration. With the melting point determined, the cooling table temperature was reduced to 253 K, whereby the system pressure dropped to 81.06 kPa. The sample did not immediately refreeze, but appeared to be a viscous supercooled liquid. The pumping line to the forepump was opened and system pressure reduced, while at the same time the temperature was reduced further. At a pressure of 2.93 kPa a nuclear crystal of solid was observed in the sample, and this subsequently grew, transforming the entire sample into the crystalline solid within a period of approximately six minutes. Pumping was continued until a pressure of 0.07 Pa was obtained. At this point the pumping lines were closed, and the system pressure immediately rose to 0.17 Pa and then continued to rise more slowly.

At a temperature of 241.1 K and pressure of 0.639 Pa, a partial melting of the sample was noted. Bubbles formed in the liquid parts and rose to the surface. There they burst, causing an increase in the rate of pressure rise. This behavior continued for approximately ten minutes during which the pressure rose to 1.5 Pa. The bubbling then ceased, and the sample again appeared to be solidly frozen in the crystalline state. It was tentatively assumed that this bubbling behavior was due to out-gassing of dissolved gasses from the sample.

The temperature of the sample was then slowly increased while close visual observation of the sample was maintained. At a temperature of 257.9 K and a pressure of 1.612 Pa definite signs of melting were observed in the sample. The data obtained during the melting of this sample are given in Table 2.

TABLE 2. LOW PRESSURE MELTING, MONOHYDRATE SAMPLE

T (K)	Pressure (Pa)	Extent of Sample Melted (Visual Estimation)
257.9	1.612	Detectable melting
262.5	1.657	25%
266.5	1.709	40%
266.8	1.761	80%

Thus a "low pressure melting point" was observed at a temperature of 266.5 K, some 15.5 K reduced from the previously measured "high pressure melting point".

While a small amount of unmelted solid yet remained in the sample, the pressure in the bell jar was increased to 65.3 kPa by the injection of dry N_2

gas. It was noted that the sample immediately began to refreeze, the solid phase growing at the expense of the liquid phase. After five minutes from the time of pressure increase, the system was judged to be approximately 40% solid at a temperature of 267.3 K and a pressure of 65.62 kPa. However, the sample did not solidly refreeze, but was extensively slushy, making a reasonable estimate of the extent of freezing difficult. After forty-five minutes from the pressure increase, the sample was seen to be composed of approximately 40% crystalline solid with the remainder appearing to be a glassy solid. It was finally decided to presume that the sample, now at temperature of 263.7 K and a pressure of 65.54 kPa, was "solidly frozen". Observations of the subsequent melting behavior described below appeared to support this presumption: the melted liquid could be visually distinguished from the glassy solid, although this distinction was admittedly more difficult than was the case when only the crystalline solid was present.

Once again the sample temperature was slowly increased, while close visual surveillance of the sample was maintained. The third observation of a melting point in this sample is detailed in Table 3.

TABLE 3. SECOND HIGH PRESSURE MELTING, MONOHYDRATE SAMPLE

T (K)	Pressure (kPa)	Extent of Sample Melted (Visual Estimation)
263.7	65.539	Solidly frozen
279.6	65.773	Definite signs of melting noted
281.5	65.796	60 - 80%
283.8	65.805	95%

From these data the melting temperature of this "second high pressure melting point" is estimated to be 281.0 ± 0.5 K. This agrees, within the combined estimated errors, with the previous melting temperature, obtained from the data of Table 1. Thus it is concluded that no substantial distillation had occurred during the course of the run, and that the final concentration of the sample was not significantly different from the initial concentration. There is definite evidence of an unexpected pressure effect on the melting point of the sample, with a reduction in pressure causing a reduction in the melting temperature.

This experimental observation is graphically presented in Figure 4. The broken line connecting the high-pressure and low-pressure apparent melting points is not intended to represent any functional relationship, but only to indicate the extent of the temperature and pressure changes between the observations.

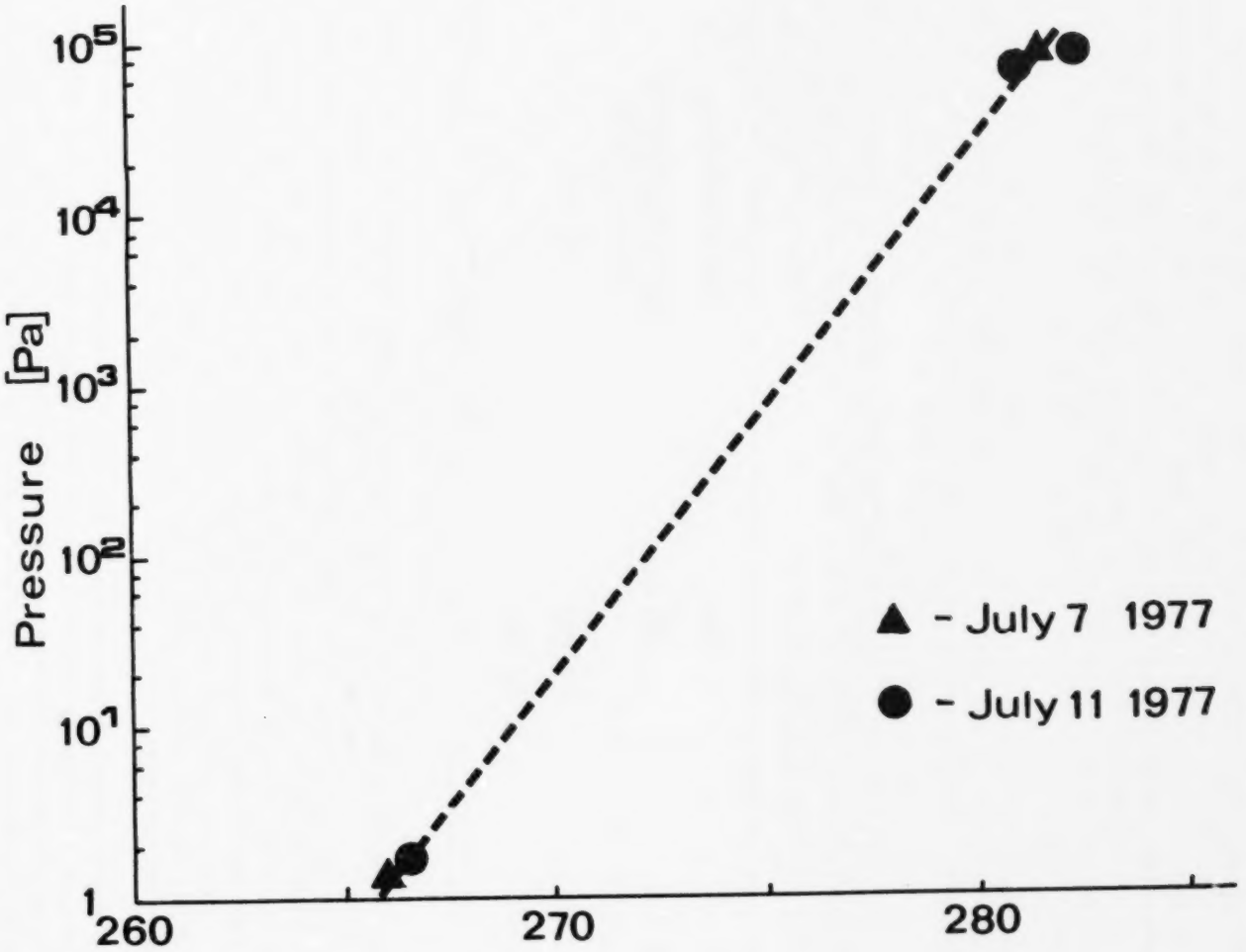


Figure 4. Apparent Pressure Effect of $H_2SO_4 \cdot H_2O$.

PRESSURE - MELTING POINT RUNS ON H_2SO_4 - H_2O NEAR 100% H_2SO_4

General

An effort was made to observe the possible pressure effect on the melting curve in samples with higher concentrations than the monohydrate. Runs using the commercial sample A-300 (95 - 98 wt% H_2SO_4) and the 100% H_2SO_4 were made on July 12, 1977 and July 13, 1977, respectively.

Run of July 12, 1977 (A-300 Sample)

A sample of H_2SO_4 - H_2O was taken directly from the A-300 commercial preparation and handled in the usual fashion: it was frozen at liquid nitrogen temperature, and transferred to the cold cooling table within the bell jar under a dry N_2 atmosphere.

The pressure within the bell jar was reduced to 79.3 kPa and the melting point was measured as described above for the monohydrate sample. The melting temperature was determined to be 255.3 ± 0.5 K. This corresponds, by Fig. 3, to a sulfuric acid concentration by weight of 95.5%, which is within the range stipulated by the manufacturer.

The temperature of the sample was then reduced to 245 K in an attempt to refreeze it. The sample did not refreeze easily. After approximately forty-five minutes the sample had only partially refrozen to a slushy consistency, and growth of the solid phase was proceeding exceedingly slowly. Since it did not appear that this sample would become solidly frozen within a reasonable time, the bell jar was evacuated while part of the sample remained liquid. As the chamber was evacuated, the solid phase in the sample at first appeared to increase in size. Then, numerous small bubbles appeared, followed by a short period of vigorous bubbling, which suddenly culminated in the complete melting of the sample.

At a temperature of 241.1 K and pressure of 0.12 Pa the sample was completely liquid, with a calm surface, and was taking on the now-familiar greenish tint. Subsequent attempts to refreeze this sample by increasing the pressure failed.

Run of July 13, 1977 (100% H_2SO_4 Sample)

A sample of approximately 2 ml in volume of the 100% H_2SO_4 sample was prepared and placed frozen on the cold cooling table inside the bell jar. It was necessary to vent the bell jar in this instance with ambient air, since the supply of dry N_2 was exhausted. At a pressure of 77.2 kPa this sample exhibited a melting point of 270 K. By Fig. 3, this corresponds to a concentration of 97.5 wt% of H_2SO_4. (It was noted that the difference from 100% H_2SO_4 could possibly have been absorbed water vapor from the air which was used to vent the bell jar.)

Subsequent to the melting of the sample, all attempts to refreeze it inside the apparatus proved futile.

OBSERVATIONS OF VAPOR BY MASS SPECTROMETER

Several spectra of the vapor of H_2SO_4 - H_2O system were obtained using the mass spectrometer. At this point, only qualitative conclusions could be drawn from the mass spectrometer data. In addition to a high water background (Mass 18), peaks at mass numbers 16, 28, 29, 48, 64, 81 were dominant. These peaks were observed with sulfuric acid concentrations near 100% by weight and also near the monohydrate concentrations. Qualitative indications from initial calibrations, point toward a definite possibility of a detailed and accurate measurement of the molecular fragments SO, SO_2, SO_3, HSO_3 etc., of the sulfuric acid - water system at varying concentrations. However, as mentioned earlier, the apparent pressure effect on the melting point of sulfuric acid has taken precedence over the quantitative study of the molecular fragments of sulfuric acid - water system with a mass spectrometer.

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